PRODUCTS OF FLASH HYDROGENATION OF ILLINOIS NO. 6 COAL

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The chemical structure of coal is still a matter of continuing speculation. All workers do agree, however, that it is indeed a fairly fragile structure which can easily be transformed into species of higher molecular weight.[1] The process is thought to be the result of the competitive reactions of fragmentation and polymerization of portions of the coal structure. Rapid heating to above 500°C improves selectivity toward lighter products by accelerating fragmentation and volatilization during the early stages of polymerization. Hydrogen acts to stabilize the light species formed by terminating free radicals which might otherwise polymerize.

Forty years ago Dent had established that raw coal can give substantial yields of gaseous hydrocarbons at high temperatures and hydrogen pressures (2-5). His work was later confirmed by researchers at Purdue University (6-9) and the Institute of Gas Technology (10).

In an effort to obtain data at shorter solids contact time, the U.S. Bureau of Mines developed a captive sample technique for rapidly heating coal to temperature (in about 2 to 4 minutes) (11,12). Other workers have also investigated the flash heating (5 seconds or less) of coal in hydrogen atmospheres with both very long (1 minute or more) (13-18), and very short (30 seconds or less) (17-24) solids residence times.

The Bureau's experiments with rapid heating established that significant liquid yields could be obtained with uncatalyzed as well as catalyzed coal by operating at moderate temperatures (700-800°C) and keeping vapor product residence times to 25 seconds or less (11,12,25-29). While those employing flash heating have obtained higher product yields, no significant liquid yields were reported (aside from a few percent heavy tars). In these experiments gas residence times were too long (13,15,17,18,20-22,24) or reaction temperatures too high (14,17-19, 23,24) for production of liquids.

The Bureau's work (with catalyzed coal) also points to the existence of an optimum vapor residence time (28). Too short a residence time does not allow conversion of heavy materials evolved from the coal to light products; too long a time results in a loss of light liquids by cracking and carbonization.

Experimental Reactor

Our reactor (Figure 1) is similar in design to the Bureau's reactor (11,12) but is capable of much higher heating rates (about one second or less to 800°C). This configuration allows for independent selection of the three important time parameters: heating rate, vapor residence time, and solids contact time. About ten milligrams of coal is deposited in the form of a thin ring on the interior surface of a 316 stainless steel tube, 0.25 inches in outside diameter, 0.20 inches in inside diameter and 12 inches long. The deposit is formed by floating ground coal on carbon tetrachloride. As the carbon tetrachloride evaporates, a deposit about 0.5 cm long is left on the tube. A quartz wool plug at the reactor outlet serves to protect the collection system downstream from particles which might be dislodged from the sample. The reactor is clamped between electrical leads and connected to a source of hydrogen on the left, and evacuated collection tanks on the right. A thermocouple is spot welded to the exterior of the reactor tube at the location of the coal sample.

Flow of hydrogen is established at the desired pressure with the reactor and inlet system at room temperature. At time zero electrical power is supplied from transformers, resistively heating the reactor tube. When a preset temperature is reached a controller switches on a holding current to maintain the desired temperature level for the duration of the experiment.

The vapor product residence time in these experiments is the time required for the products evolved from the coal to be carried by the flow of hydrogen to the right hand electrical lead. Because of its large mass, the lead remains at its initial temperature and serves as the quench point. Variations in vapor residence time are achieved by changes in location of the coal ring or in rate of hydrogen flow.

Following hydrogenation the residual char is burned in situ with oxygen at four atmospheres and the oxidation products collected in a separate tank for analysis.

Analyses are performed with a gas chromatograph using a Poropak-Q column for all hydrocarbons and carbon dioxide and a molecular sieve column for carbon monoxide.

Coal Sample

The yields reported here were obtained with a mine-mouth sample of Illinois No. 6 coal. The sample was crushed and ground in air to less than 325 mesh and subsequently stored under nitrogen. The ultimate analysis (weight percent, moisture free) is as follows:

carbon	68.2%
hydrogen	5.1%
nitrogen	1.1%
sulfur	4.2%
oxygen (by difference)	9.3%
ash	12.1%

Exploratory Runs

The influence of heating rate, solids contact time and vapor pro-
duct residence time were explored in a series of preliminary experi-
ments to provide a basis for planning the more extensive study. All
runs are in hydrogen at 100 atmospheres.

From the preliminary study we tentatively conclude that a heat-
ing rate of 650°C per second is sufficiently high and a solids contact
time of ten seconds sufficiently long to characterize the products of
flash hydrogenation. Increasing the heating rate to 1400°C per second
provides the same yields. Heating at 20°C per second with a solids
contact time of 65 seconds results in a three-fold decrease in single
ring aromatics and a substantial increase in heavier species. Yields
at 30 seconds solids contact time are substantially the same as at 10
seconds when the heating rate is 650°C per second. Shortening the
solids contact time to two seconds results in slightly reduced yield
of all light species.

Tests at different vapor product residence times show that there
is an optimum value for this parameter for yield of light aromatics.
For example, in the vicinity of 800°C the BTX (benzene + toluene +
xylene) yields are lower both at 0.18 seconds and 23 seconds than at
0.6 seconds.

Yield Structure

On the basis of the preliminary runs, reaction temperature and
vapor residence time were selected as variables for more detailed
study. Heating rate was fixed at 650°C per second and solids contact
time at 10 seconds. The influence of reaction temperature was explored
from 620 to 980°C with a vapor product residence time of 0.6 seconds
(Figures 2-5). The influence of vapor product residence time was ex-
plored from 0.6 to 5 seconds at a temperature of 700°C (Figures 6-8).

Carbon Balance

The principal products observed are methane, ethane, propane,
benzene, toluene and xylenes. Other species, such as butanes, ethylene
and propylene are found only in trace amounts (less than 1 percent).
Tests of the collection system were made by injecting known quantities
of components ahead of the reactor. Xylene and lighter species are
recovered quantitatively.

A carbon balance is made by summing the carbon content of the observed hydrogenation and combustion products (the latter is CO_2 with minor amounts of CO). The difference between the carbon recovered and the carbon content of the weighed coal sample is reported as carbon deficit in Figures 2 and 6.

These figures suggest that the light hydrocarbons directly measured substantially account for the products of flash hydrogenation at temperatures beyond 850°C at 0.6 seconds residence time (Figure 2) and at residence times beyond 3 seconds at 700°C (Figure 6). The scatter in carbon deficit is low. For the 19 runs reported, the precision (95% confidence level) is $\pm3\%$.

The carbon deficit at lower temperatures in Figure 2 and shorter residence times in Figure 6 is attributed to species heavier than xylene.

Effect of Reaction Temperature

Carbon conversion to methane (Figure 3) increased from 5% at 620°C to 38% at 980°C. In contrast, carbon conversion to propane (Figure 4) falls quickly from 2% at 620°C to nearly zero at 780°C. Ethane (Figure 4) shows a peak yield near 760°C of 6.8%. By 940°C the ethane drops to an insignificant level.

Little BTX (Figure 5) appears below 620°C. The yield peaks at 800°C with a conversion of 11.6% and drops to 3% at 980°C. Benzene is 41% of the BTX mixture at 620°C. The fraction rises steeply with temperature and beyond 790°C the mixture is nearly pure benzene.

Effect of Vapor Product Residence Time

The effect of increasing vapor product residence time at 700°C is shown in Figures 6-8. At this temperature and 0.6 seconds, 12% of the carbon in the coal is converted to material heavier than xylene. With increasing residence time the yield of this material decreases, vanishing at 3 seconds (Figure 6).

These heavy species are converted to methane, ethane, BTX, and coke. At 3 seconds methane has increased by 5.5%, ethane by 2% and BTX by 5%. Beyond 3 seconds ethane remains nearly constant while methane and BTX decline. This is accompanied by an increase in char deposited on the reactor walls downstream of the coal sample.

Implications

The principal result of the studies reported here is to demonstrate that heavy species evolved from coal by flash heating in hydrogen at

elevated pressure are of such character as to be quickly converted to BTX and light alkanes in the vapor phase. It is significant that little if any tars are produced. Going to higher temperatures results in the formation of even lighter species with temperatures 700 to 800°C being optimum for production of BTX.

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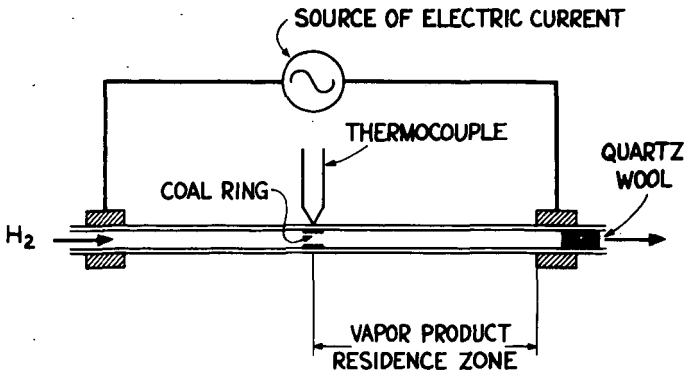
Figure 1. Reactor for flash heating of coal. Location of coal
   deposit and hydrogen flow rate are selected to give the desired
   vapor product residence time.

Figures 2-5. Yields versus temperature at 100 atm. H_2, heating rate
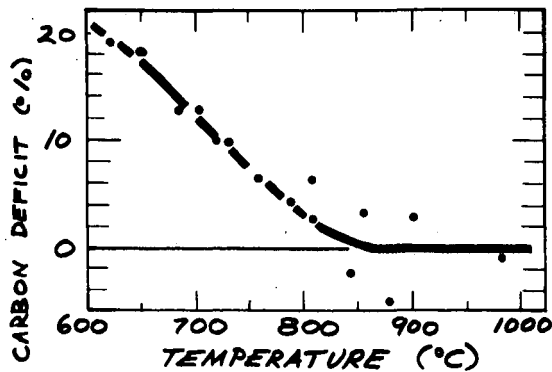 $650°C/sec$, 0.6 sec. vapor residence time, 10 sec. solids contact
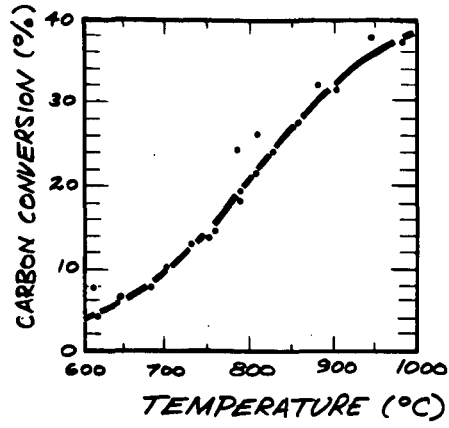   time.
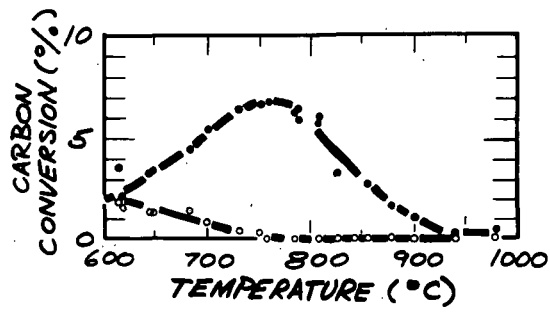

Figure 2. Carbon deficit.

Figure 3.   Methane Yield

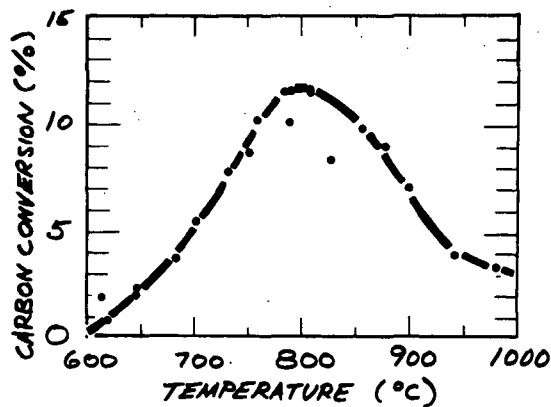Figure 4. Yield of ethane (closed circles) and propane (open circles).

Figure 5. BTX (benzene + toluene + xylenes) yield.

Figures 6-8. Yields versus vapor residence time at 700°C, 100 atm.
hydrogen, heating rate 650°C/sec., 10 sec. solids contact time.
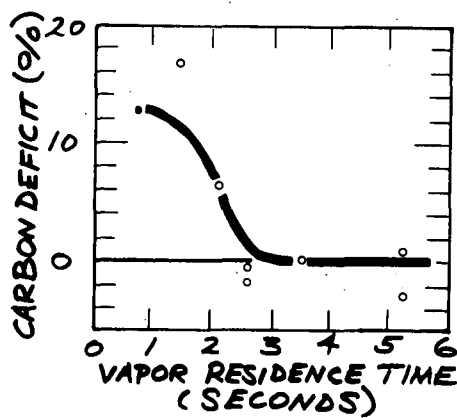(Closed circles from Figures 2-5.
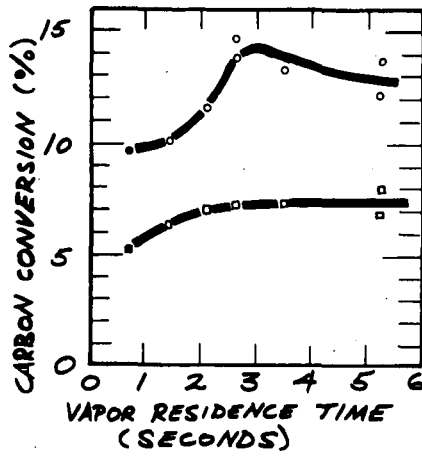

Figure 6. Carbon deficit.

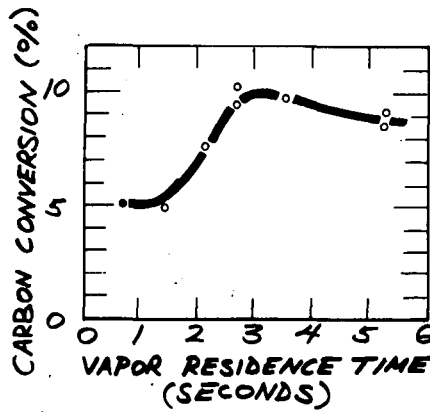Figure 7. Yields of methane (circles) and ethane + propane (squares)

Figure 8. Benzene yield.